

Single-Laboratory Evaluation and Modification of
U.S. EPA (Environmental Protection Agency)
Methods 7470 and 7471 for the Determination of
Mercury in Aqueous and Solid Hazardous Wastes
(Journal Version)

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16. ABSTRACT The current U.S. Environmental Protection Agency (U.S. EPA) protocols for mercury determinations in aqueous and solid waste samples (SW-846 Methods 7470 and 7471) have been modified in a single-laboratory study to facilitate additional QC measures, to enhance detectability for low-level mercury concentrations, and to eliminate nonspecific vapor absorption interferences. Volumetric manipulations for additional QC measures, if required, are facilitated by performing the sample digestions in Erlenmeyer flasks rather than in the current Biochemical Oxygen Demand (BOD) reduction-aeration bottles. Instrument detectability is improved 10-fold by using a gas sparging bottle as a dedicated reduction-aeration vessel and a silver wool-amalgamation CV-AAS system operated in an open configuration. The on-line amalgamation/thermal desorption process of the modified CV-AAS system eliminates interfering water and organic matrix vapors prior to the mercury absorption measurement. Good accuracy and precision have been obtained with the amalgamation CV-AAS system for the analyses of four reference sediment materials. <i>(Copyright)</i> <i>(1988 Pergamon Press)</i>		
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SINGLE-LABORATORY EVALUATION AND MODIFICATION OF U.S. EPA METHODS 7470 AND 7471 FOR THE DETERMINATION OF MERCURY IN AQUEOUS AND SOLID HAZARDOUS WASTES

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The current U.S. Environmental Protection Agency (U.S. EPA) protocols for mercury determinations in aqueous and solid waste samples (SW-846 Methods 7470 and 7471) using recirculating cold-vapor atomic absorption spectrometry (CV-AAS) have been evaluated. The U.S. EPA methods are not sufficiently flexible to permit special quality control (QC) measures, have limited detectability for low-level mercury concentrations, and are plagued by spectral interferences caused by the nonspecific absorption of primary mercury radiation by volatile organic vapors. The U.S. EPA protocols have been modified in a single-laboratory study to facilitate additional QC measures, to enhance detectability for low-level mercury concentrations, and to eliminate nonspecific vapor absorption interferences. Volumetric manipulations for additional QC measures, if required, are facilitated by performing the sample digestions in Erlenmeyer flasks rather than in the current Biochemical Oxygen Demand (BOD) reduction-aeration bottles. Typical manipulations for additional QC measures that are now feasible include dilution of concentrated samples and multiple aliquot sampling for post-digestion spike and replicate analyses. Instrument detectability is improved 10-fold by using a gas sparging bottle as a dedicated reduction-aeration vessel and a silver wool-amalgamation CV-AAS system operated in an open configuration. The on-line amalgamation/thermal desorption process of the modified CV-AAS system eliminates interfering water and organic matrix vapors prior to the mercury absorption measurement. Good accuracy and precision have been obtained with the amalgamation CV-AAS system for the analyses of four reference sediment materials. The amalgamation CV-AAS measurements on the reference sediment digests have been successfully performed at absolute mercury concentration levels that are only 1 to 4 times above the instrumental detection limit of the U.S. EPA recirculating CV-AAS method.

Introduction

Two analytical protocols for the determination of mercury in aqueous and solid waste materials, U.S. EPA Methods 7470 and 7471, are described in the second edition of Publication SW-846 ("Test Methods for Evaluating Solid Waste," 1982). The analytical methodologies are implemented to characterize hazardous waste materials for total mercury content for regulation under the Resource Conservation and Recovery Act (RCRA).

Method 7470 is designed for the determination of total mercury in mobility procedure extracts, aqueous wastes, and ground waters. The samples are digested on a steam bath with sulfuric acid, nitric acid, and

permanganate to oxidize sulfides, and then with persulfate to oxidize organics. Method 7471 is designed for the determination of total mercury in soils, sediments, bottom deposits, and sludge-type materials. In Method 7471, the samples are digested on a steam bath with aqua regia, and then with permanganate to oxidize any remaining sulfides. Method 7471A is an alternative sample preparation procedure for Method 7471. In Method 7471A, the samples are digested with a mixture of sulfuric acid, nitric acid, and permanganate under heat and pressure in an autoclave. The addition of persulfate to degrade organomercuric compounds is not specified in Methods 7471 and 7471A. In all the methods, excess permanganate, persulfate, or

any free chlorine present in the sample digests are reduced with a hydroxylamine salt. After the reduction of mercuric ions in solution with a stannous salt, elemental mercury is aerated from the solution. The mercury vapor is then continuously recirculated in a closed system through the absorption cell of an atomic absorption spectrophotometer until a steady-state absorption signal is attained for quantification. The discrete cold-vapor atomic absorption spectrometric (CV-AAS) technique incorporated into Methods 7470 and 7471 is based on the recirculating CV-AAS configuration (Hatch, 1968) originally designed for mercury determinations in metallurgical, geological, and soil samples.

The potential interferences with the CV-AAS measurements for mercury include: (1) incomplete recoveries of total mercury from samples containing sulfide, copper, and organomercuric compounds, and (2) spectral interferences which are due to nonspecific absorption of the primary mercury radiation that may occur with volatile organic vapors or chlorine gas formed from the oxidation of chloride matrix ions. Quantitative recoveries of inorganic and organic forms of mercury from water and sediments have been achieved with digestion mixture combinations of acids and oxidizing agents (Jacobs, 1974; Agemian, 1975; El-Awady, 1976; Jirka, 1978; Agemian, 1978; Randlesome, 1980). Signal suppressions caused by the precipitation or amalgamation of mercury with selected metals in the sample digests during the reduction-aeration step under certain conditions have been alleviated by using an alkaline sodium borohydride reductant alone (MacPherson, 1982) or in the presence of EDTA complexing agent (Bernth, 1984). In addition to persulfate oxidation, organomercurials have been effectively decomposed by ultraviolet degradation (Agemian, 1978), alkaline permanganate digestion (Chapman, 1982), and hydrochloric acid-permanganate or bromine monochloride digestions (Szakacs, 1980). Organomercuric species in the sample digests or extracts have also been determined directly by reduction with alkaline tin(II) solution (Matsunaga, 1976) or with alkaline sodium borohydride solution (Oda, 1981).

In the present protocols of Methods 7470 and 7471, such interferences are assumed to be effectively eliminated by the sample digestion/reduction methods; multiplicative interferences that remain are compensated for by the method of multiple standard additions (MSA). However, if volatile organic vapors or residual chlorine gas remain in the sample digests, no approach to instrumental background correction for nonspecific absorption is designated. To compensate for the presence of chlorine gas, Methods 7470 and 7471 recommend that an excess of the hydroxylamine reductant solution be added, and that the dead air space in the BOD bottle be purged before the addition of the tin(II) reductant solution. To correct for the presence of vol-

atile organic compounds in the sample digests which are not oxidized during the digestion procedure, Methods 7470 and 7471 recommend that a preliminary blank analysis of the sample be performed under oxidizing conditions without the addition of the reductant solutions; the corrected mercury absorbance is obtained by subtracting this blank absorbance from the total sample absorbance obtained when the sample is analyzed under the normal reducing conditions.

Many research efforts involving the CV-AAS method have focused on the identification and optimization of the critical variables affecting sensitivity and peak shape (Hawley, 1975; Koirtiyohann, 1976; Stuart, 1979; Donard, 1983). Practical strategies include reducing the dead volume of the CV-AAS apparatus, increasing the efficiencies of the reduction of mercuric ions and the diffusion of elemental mercury vapor into the carrier gas stream, optimizing the reagent concentrations and volumes, and optimizing the carrier gas flow rates and instrumental parameters. The sensitivity of the CV-AAS method has been increased by modifying the geometry of the reduction-aeration vessel (Ramelow, 1977), by heating the reduction-aeration vessel (Carrillo Camarero, 1984; Carrillo, 1986), and by magnetic stirring of the sample solution (Narasaki, 1977). The sensitivity of the technique has also been increased by optimizing the geometry of the absorption cell (Hawley, 1975; Ramelow, 1977; Tuncel, 1980; Donard, 1983; Carrillo Camarero, 1984; Sturman, 1985; Carrillo, 1986).

Because water vapor is produced during the reduction-aeration step of the CV-AAS method, a magnesium perchlorate desiccant is usually incorporated into the cold-vapor generator apparatus as a moisture trap to prevent interferences caused by water condensation on the end-windows of the absorption cell. However, the desiccant may absorb mercury, introduce variable memory effects and contamination, and broaden absorption peaks; an additional inconvenience is that frequent changing of the desiccant medium is required. To alleviate water vapor interferences without incurring the problems of a magnesium perchlorate desiccant, a heated absorption cell (Christmann, 1976) and a windowless absorption cell (Velghe, 1977) have been utilized in some CV-AAS designs.

A single-laboratory evaluation of the current U.S. EPA protocols for Methods 7470 and 7471 has been conducted in the present study to identify any phase of the CV-AAS technique which could be modified for potential improvement in the accuracy and precision of mercury quantification. The sample preservation and digestion procedures in Methods 7470 and 7471 were used without significant modification. To increase sensitivity and to eliminate nonspecific absorption interferences, the recirculating CV-AAS technique in Methods 7470 and 7471 was converted to an

Table 1. Apparatus and parameters for recirculating CV-AAS.

Component	Description
Spectrophotometer	Perkin-Elmer Model 603
Signal	Concentration
Mode	Peak height
Recorder	TC1 (1 second time constant)
Background Corrector	Off
Slit Width	1 mm (0.7-nm spectral bandpass)
Wavelength	253.7 nm
Grating	Ultraviolet (2880 lines/mm)
Integration Time	120 seconds
Light Source	Mercury hollow cathode lamp
Lamp Current	6 mA
Absorption Cell	11.5 cm, 2.5-cm o.d., absorption cell with fused silica windows
Recorder	Hitachi Ltd. Model 056-1005
Air Pump	Neptune Dyna-Pump Model 4K
Flowmeter	Brooks Tube
Tubing	Tygon™ (6.4 mm i.d.)
Reduction-Aeration Vessel	300-mL BOD bottle (2-hole rubber stopper)

open CV-AAS configuration which incorporated an on-line amalgamation/thermal desorption process. Mercury vapor aerated from solution in a dedicated gas sparging bottle was preconcentrated onto silver wool; water vapor and volatile matrix species were purged from the system prior to the mercury absorption measurement. The open CV-AAS method with the on-line amalgamation/thermal desorption process was adapted from an amalgamation method previously developed for the determination of mercury in ambient air (Long, 1973).

Commercial or customized variations of on-line amalgamation/thermal desorption designs for mercury preconcentration represent an established and modern CV-AAS approach which has found increased use in many analytical laboratories. Preconcentration and separation of mercury from the sample matrix have been accomplished with a variety of amalgamating media including silver wool (Long, 1973; Murphy, 1975; Dogan, 1978), silvered alumina (Taylor, 1983), gold (Wimberley, 1975; Konishi, 1983), gold/platinum gauze (Welz *et al.*, 1984; Welz and Melcher, 1984), and copper (Dogan, 1976; Dogan, 1979).

In the present study, the critical operating parameters of the on-line amalgamation/thermal desorption process for selective preconcentration of mercury on silver wool were optimized and tested for ruggedness. The amalgamation CV-AAS method was compared to the current U.S. EPA recirculating CV-AAS method for the determination of mercury in the presence of volatile organic compounds. The amalgamation CV-AAS method was further tested for the recovery of total mercury from selected organomercuric compounds and from inorganic matrices containing sulfide,

copper, and chloride ions. The accuracy and precision of the amalgamation CV-AAS method for trace concentrations of mercury were assessed by the analyses of four sediment reference materials.

Experimental

Apparatus

A Model 603 atomic absorption spectrophotometer (The Perkin-Elmer Corporation, Norwalk, CT, USA), modified to accommodate either a recirculating or an amalgamation cold-vapor generator apparatus, was used for all analytical measurements. Although a mercury hollow cathode lamp was used in this study, a mercury electrodeless discharge lamp (EDL) would also serve as a suitable primary spectral line source. A cylindrical glass absorption cell, with entrance and exit ports on the side and quartz end-windows, was mounted on a conventional burner head assembly for convenient positioning and two-dimensional alignment in the optical path of the spectrophotometer. Tygon™ tubing was used for all glass-to-glass connections. The signal response for each system was monitored simultaneously on the digital display of the spectrophotometer and on a strip-chart recorder with a nominal one-second time constant. Peak-height signal measurement was used exclusively.

Recirculating CV-AAS. The recirculating CV-AAS apparatus designated in Methods 7470 and 7471 was assembled without significant modification from components and materials as specified in the current protocols. The apparatus and relevant operating parameters are listed in Table 1; a schematic diagram of the recirculating CV-AAS system is illustrated in Fig.

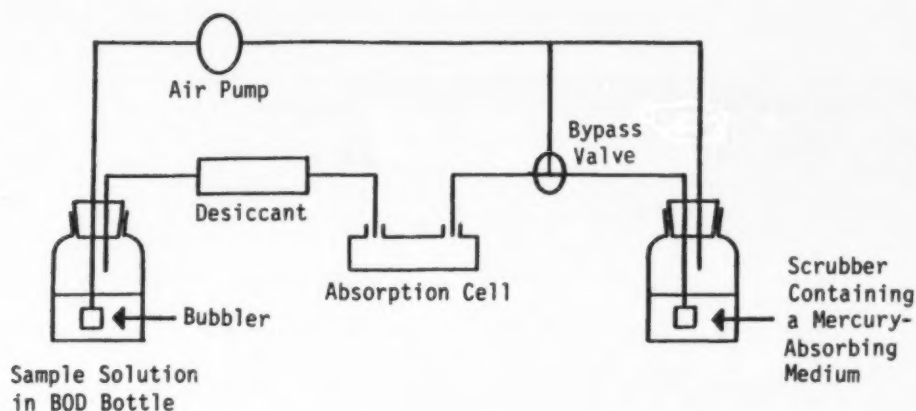


Fig. 1. Apparatus for the recirculating CV-AAS method.

1. Instead of passing the mercury vapor through a mercury-absorbing medium at the end of the analysis, the mercury vapor could also be vented appropriately into an exhaust hood.

A portable lamp with a light shield was clamped to the exhaust hood and positioned four inches above the absorption cell; the incandescence from the lamp heated the air within the absorption cell to slightly above ambient temperature, thus preventing the condensation of water vapor on the end windows. With this configuration, the magnesium perchlorate desiccant in the flow-path position between the reduction-aeration vessel and the absorption cell, as illustrated in Fig. 1, was not required.

Amalgamation CV-AAS. The recirculating CV-AAS apparatus was modified in an inexpensive manner to incorporate three significant changes: (1) the recirculating ambient air train was converted to an open "once-through" nitrogen purge system, (2) the individual 300-mL BOD bottles were replaced with a single 125-mL gas sparging bottle as a dedicated reduction-aeration vessel, and (3) on-line preconcentration was incorporated in which mercury vapor aerated from solution in the reduction-aeration vessel is preconcentrated by amalgamation onto silver wool, is thermally desorbed, and then is purged into the absorption cell. The replacement of the recirculating ambient air train with a flow-through nitrogen purge eliminated the need for the air pump and mercury scrubber medium. The replacement of the BOD bottle with a standard gas sparging bottle improved the geometry of the reduction-aeration vessel for the rapid aeration of mercury vapor from solution; the improved efficiency of aeration of mercury vapor from solution reduced the time required for preconcentration. The incorporation of on-line preconcentration on silver wool increased the sensitivity of the mercury absorption measurement and permitted an intermediate purging of the gas train between the mercury

preconcentration and thermal desorption steps. The intermediate purge eliminated from the system any water vapor or volatile organic compounds which could contribute to nonspecific background absorption during the mercury absorption measurement so that desiccants or automatic instrumental background correction were not required.

The apparatus and relevant operating parameters for amalgamation CV-AAS are listed in Table 2. The individual components of the amalgamation CV-AAS apparatus are discussed below in the order as they appear in the schematic diagram in Fig. 2.

Compressed nitrogen gas, commercial grade or better, was used as the purge gas. The nitrogen purge gas flow rate was controlled by adjustment of a needle valve connected to the outlet of the nitrogen cylinder pressure regulator. Potential mercury and organic vapor contamination was removed from the nitrogen purge gas by an activated charcoal trap. The nitrogen purge gas flow rate of approximately 0.5 L/min was monitored with a Leco Tube flowmeter calibrated for nitrogen gas.

The reduction-aeration vessel was a glass (Kimax) 125-mL gas sparging bottle attached via ground glass connections to a straight glass bubbling tube with an end-frit of coarse porosity. The reduction-aeration vessel was positioned in one of two alternate flow paths in the nitrogen purge gas train. The direction of the flow of nitrogen through the purge gas train was controlled by a glass stopcock bypass valve. To inhibit excessive foaming by the organic constituents present in some environmental samples, the upper one-inch portion of the inner wall of the sparging bottle and the upper one-inch segment of the aeration tube were coated with a film of silicone lubricant high-vacuum grease (Dow Corning Corporation, Midland, MI, USA).

The silver-wool collection tube was a 100-mm long,

Table 2. Apparatus and parameters for amalgamation CV-AAS.

Component	Description
Spectrophotometer	Perkin-Elmer Model 603
Signal	Concentration
Mode	Peak height
Recorder	TC1 (1 second time constant)
Background Corrector	Off
Slit Width	1 mm (0.7-nm spectral bandpass)
Wavelength	253.7 nm
Grating	Ultraviolet (2880 lines/mm)
Integration Time	45 seconds
Light Source	Mercury hollow cathode lamp
Lamp Current	6 mA
Absorption Cell	16 cm, 2.5-cm o.d., absorption cell with fused silica windows
Recorder	Hitachi Ltd. Model 056-1005
Flowmeter	Leco Tube
Tubing	Tygon™ (6.4 mm i.d.)
Silver Wool	Micro-analysis grade (0.7-g plug)
Chromel-A Wire	100 cm, 22 gauge
Reduction-Aeration Vessel	KIMAX 125-mL sparging bottle (34/28)
Resistance Heating Power Supply	5-watt Variac autotransformer

5-mm i.d., borosilicate glass tube with end ball joints. The collection tube contained a glass dimple (facing inward) located 10 mm off-center with respect to tube length. Approximately 100 cm of 22-gauge Chromel-A resistance heating wire was tightly wound around the outside of the tube in order to cover the centermost 40 mm of tube length with approximately 30 windings. To ensure uniform heating, the windings were evenly spaced and were not allowed to touch or overlap.

The micro-analysis grade silver wool (Fisher Scien-

tific Company, Fair Lawn, NJ, USA) was initially cleaned by heating in a muffle furnace at 800°C for 2 hours. The 0.7-g portions used for amalgamation were inserted into the longer end of the collection tube, as referenced by the glass dimple. The silver wool was gently forced through the tube against the glass dimple and was compressed to a length of approximately 20 mm. When properly positioned, both the silver wool and the Chromel-A wire wrappings were centered with respect to the length of the tube. For the resistance

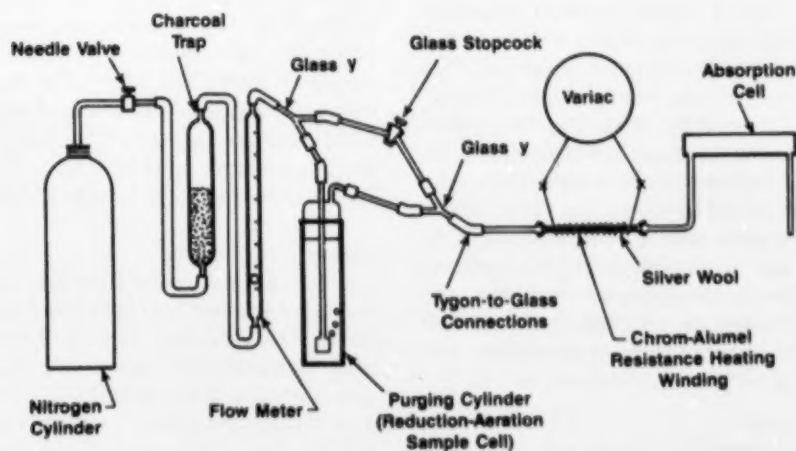


Fig. 2. Apparatus for the amalgamation CV-AAS method.

heating step, both ends of the Chromel-A wire were connected to the leads of a 5-watt Variac autotransformer.

The silver-wool collection tube was inserted in the nitrogen gas flow train so that the glass dimple was downstream of the 0.7-g silver-wool plug; the collection tube was immobilized with ball joint clips on both ends. In this configuration, the glass dimple secures the silver-wool plug from slippage caused by the positive pressure of the nitrogen purge gas.

A cylindrical glass absorption cell, 2.5 cm in diameter (o.d.) and 16 cm in length, was found to have a suitable geometry; the length was increased by approximately 4.5 cm over the length of the absorption cell specified for the U.S. EPA recirculating CV-AAS apparatus. A TygonTM tube, connected to the outlet port of the absorption cell, was attached to the inside of an exhaust hood to vent the mercury vapor after it had passed through the absorption cell.

Reagents

Mineral acids, inorganic reagents, and organic solvents were of ACS grade or better; no attempt was made to improve the purity of the reagent solutions or acids before use. Approximately 5 ng of mercury was determined in the digested reagent blanks for the reagent volumes specified in Methods 7470 and 7471.

Inorganic mercury working standards were prepared fresh daily by serial dilutions with deionized water from a commercial 1000 mg/L mercury stock solution (Fisher Scientific Company, Fair Lawn, NJ, USA). Acidity of the working standards was maintained with 0.15 percent (v/v) nitric acid. Methyl mercuric chloride standards were prepared by dilution with deionized water from a stock solution previously prepared from the commercial solid material (Pfaltz and Bauer, Inc., Waterbury, CT, USA). Diphenyl mercury standards were prepared by dilution with chloroform from a stock solution previously prepared from the commercial solid material (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). A 5-percent (w/v) potassium permanganate solution was prepared by dissolving 50 g potassium permanganate in deionized water and then by diluting to 1 L. A 5-percent (w/v) potassium persulfate solution was prepared by dissolving 50 g potassium persulfate in deionized water and then by diluting to 1 L. A sodium chloride-hydroxylamine hydrochloride solution was prepared by dissolving 120 g sodium chloride and 120 g hydroxylamine hydrochloride in deionized water and then by diluting to 1 L. A 15-percent (w/v) stannous chloride dihydrate solution was prepared by carefully dissolving 150 g stannous chloride dihydrate in 300 mL concentrated hydrochloric acid and then by diluting with deionized water to 1 L.

Environmental samples

Two aqueous and four solid environmental samples were used to evaluate the recirculating and amalga-

tion CV-AAS systems for environmental analyses. A simulated aqueous sample and solid environmental reference samples of homogeneous and known compositions were employed in order to assess the relative accuracies and precisions of the CV-AAS methods without introducing uncertainties caused by sample heterogeneities.

A simulated aqueous waste sample was used for the evaluation of Method 7470. The aqueous waste sample was prepared by decanting the small aqueous fractions from three duplicate sludge-type waste samples, received from the U.S. EPA Quality Assurance Materials Bank, to form a single pooled aqueous waste sample. The pooled aqueous sample was filtered, spiked with 200 µg of mercury as mercuric chloride, acidified to less than pH 2 with nitric acid, and diluted with laboratory tap water to a 2-L volume. The simulated aqueous waste sample had a final mercury concentration of approximately 110 µg/L because of the combined endogenous and spiked mercury levels.

A natural water sample from the Olentangy River in central Ohio was also employed in one study to facilitate assessment of inorganic mercury spike recoveries by Method 7470. A 2.5-L water sample containing suspended matter was collected in an acid-washed bottle. The sample was immediately acidified with 25 mL concentrated nitric acid, and was refrigerated at approximately 4°C for 2 days before filtration. A 1-L portion of the acidified river water was vacuum-filtered through 0.22-µm Millipore filter membranes (Type GS) immediately before analysis. No endogenous mercury was detected in the filtered river water sample by amalgamation CV-AAS.

Four freeze-dried sediments, including two Standard Reference Materials (SRMs) from the National Bureau of Standards (NBS, Gaithersburg, MD, USA) and two reference materials from the National Research Council of Canada (NRCC, Ottawa, Ontario, Canada), were used to evaluate Method 7471. These reference sediment materials were River Sediment (NBS-SRM 1645), Estuarine Sediment (NBS-SRM 1646), Marine Sediment (NRCC MESS-1), and Marine Sediment (NRCC BCSS-1). The certified or reference mercury concentrations ranged from 0.063 µg/g (NBS-SRM 1646) to 1.1 µg/g (NBS-SRM 1645), with intermediate mercury concentrations of 0.129 µg/g (NRCC BCSS-1) and 0.171 µg/g (NRCC MESS-1).

Labware preparation

Glassware was initially washed with a hot, tap-water detergent solution and was then rinsed with deionized water. The glassware was filled with 25-percent (v/v) reagent-grade nitric acid solution, was soaked for a minimum of 4 hours at ambient temperature, and was then rinsed with copious amounts of deionized water. Watch glass covers and plastic tips for Finn pipets were soaked under the same conditions in beakers con-

taining 25-percent (v/v) nitric acid solution, and they were then rinsed with copious amounts of deionized water.

Sample preparation

Methods 7470 and 7471 were employed with only minor modifications for the digestions of aqueous and solid samples, respectively. To facilitate dilutions of environmental samples with high mercury content, all sample digestions were performed in glass 125-mL Erlenmeyer flasks with watch glass covers instead of in the 300-mL BOD bottles specified for digestion and reduction-aeration in Methods 7470 and 7471. Because of the analytical concerns for greater sample heterogeneity in milligram test samples of typical environmental waste materials, dilutions of concentrated sample digests are preferred to digestions of smaller sample sizes as a means of adjusting the final mercury concentration within the linear dynamic range of the CV-AAS method.

When Method 7470 was used, aqueous samples were digested on a steam bath with sulfuric and nitric acids, potassium permanganate to oxidize sulfides, and potassium persulfate to oxidize organics. When Method 7471 was used, solid samples were digested on a steam bath with aqua regia, and this was followed by additional digestion with potassium permanganate to oxidize any remaining sulfides. The autoclave digestion protocol in Method 7471 (designated as Method 7471A) was employed as an alternative digestion procedure for some analyses of solid samples. Solid samples were digested with a mixture of sulfuric acid, nitric acid, and potassium permanganate under pressure in an autoclave. A modification to the autoclave digestion protocol included the addition of 5 mL deionized water to 0.2-g solid samples before the additions of the concentrated acids. The initial addition of deionized water reduced foaming and spattering that occurred when the concentrated acids were added directly to some solid samples.

A reagent solution of sodium chloride-hydroxylamine hydrochloride was added to reduce excess potassium permanganate and manganese dioxide which had formed from the reduction of permanganate and had adhered to the walls of the flask. After turning clear and colorless upon swirling, the sample digests were transferred to 100-mL volumetric flasks for dilution or directly to the reduction-aeration vessel for analysis.

CV-AAS measurements

Following preparation and digestion of the samples using either Method 7470 or Method 7471, an aliquot of the sample digest was transferred to the 300-mL BOD bottle or to the 125-mL gas sparging bottle of the cold-vapor generator apparatus, and was then diluted to 100 mL with deionized water. After stannous chloride solution was added to reduce the mercuric

ions in solution to elemental mercury, the BOD bottle or gas sparging bottle was immediately connected to the cold-vapor generator apparatus for the mercury determination.

Recirculating CV-AAS. A 120-second, pre-programmed atomic absorption measurement was immediately initiated after connecting the bubbler tube fitting (2-hole rubber stopper) to the BOD bottle. The "steady-state" absorbance peak maximum occurred approximately 60 seconds after the BOD bottle was connected to the cold-vapor generator apparatus.

Amalgamation CV-AAS. Prior to initiating the reduction-aeration process, the nitrogen purge gas flow was directed through the open bypass valve instead of through the gas sparging bottle of the cold-vapor generator apparatus. The out-flow end of the silver-wool collection tube in the gas flow train was also disconnected from the absorption cell by removing the end ball joint clip. After connecting the sample sparging bottle to the cold-vapor generator apparatus, the nitrogen purge gas flow was redirected through the gas sparging bottle by closing the glass stopcock bypass valve. The gas sparging bottle was purged with nitrogen gas, and mercury was preconcentrated onto the silver wool for exactly 2 minutes. By bubbling nitrogen gas through the sample in the sparging bottle, mercuric ions in solution and the stannous chloride reductant were efficiently mixed to promote rapid aeration of elemental mercury vapor from solution into the nitrogen purge stream for amalgamation onto silver wool. After the 2-minute amalgamation step, the dry nitrogen purge gas flow was redirected through the bypass valve for 15 seconds to flush any residual water vapor and volatile organics from the gas flow train before the thermal desorption step and mercury absorption measurement. The out-flow end of the silver-wool collection tube was then connected to the absorption cell in preparation for the thermal desorption process. With nitrogen gas flowing through the absorption cell, the baseline was zeroed by the auto-zero function on the spectrophotometer.

After the nitrogen purge gas had been directed through the bypass valve for 1 minute, the Variac autotransformer and the strip-chart recorder were turned on, and a pre-programmed atomic absorption measurement of 45-second duration was initiated on the spectrophotometer. By resistance heating of the Chromel-A wire wrapped around the silver-wool collection tube, the preconcentrated elemental mercury was thermally desorbed from the silver-wool plug and was swept into the absorption cell by the nitrogen purge gas. While the absorbance profile was monitored on the strip-chart recorder, the maximum peak height absorbance during the 45-second period was displayed on the digital readout of the spectrophotometer. The mercury absorption peak maximum occurred approximately 30 seconds after the gas sparging bottle was

connected to the cold-vapor generator apparatus. After the peak height absorbance had decreased to approximately 0.01 absorbance unit, the Variac autotransformer and strip-chart recorder were turned off. The silver-wool collection tube was cooled in preparation for the next sample by directing a small stream of compressed air over the outside of the glass tube for approximately 2 minutes. To disperse the compressed air uniformly over the tube length wrapped with Chromel-A wire, the cone of a small funnel connected to the outlet tubing of the compressed air supply was gently rested on the collection tube during the cooling period.

The silver-wool plug was replaced when increased imprecision or an appreciable loss in sensitivity was observed as ascertained from day-to-day and within-day analyses of calibration and control check standards. With extended use, the silver wool may become contaminated by reaction with sample digest constituents aerated from the sample solution during the reduction-aeration step. If the surface characteristics of the silver wool are adversely affected, the thermal release of elemental vapor from the amalgam may become more diffuse, and this would result in absorbance peak broadening, reduced absorbance peak maximum, and degraded precision. Instrument performance was monitored by keeping a log book with pertinent absorbance data relevant to absorbance profiles and maximum absorbance peak heights to facilitate evaluation of daily instrument operation. A silver-wool plug typically lasted for one week of daily operation.

Results and Discussion

Amalgamation CV-AAS parameter optimization and ruggedness

Four operating parameters of the customized amalgamation CV-AAS system required optimization and ruggedness testing: (1) nitrogen purge gas flow rate, (2) time required for the preconcentration of mercury on silver wool, (3) Variac autotransformer voltage setting, and (4) weight of the silver wool. The selected criteria for optimization represented a compromise based on maximizing the sensitivity of the mercury absorption measurement while minimizing the time of analysis.

The nitrogen purge gas flow rate affects the two chemical processes governing the sensitivity of the atomic absorption measurement. First, the nitrogen flow rate, in conjunction with the time allowed for silver wool preconcentration, determines the amount of mercury aerated from the sample solution in the sparging bottle to be deposited on the silver wool. Second, the nitrogen flow rate, in conjunction with the Variac voltage setting, determines the rate of mercury desorption from the silver wool. As the most critical step in an amalgamation system, the thermal desorp-

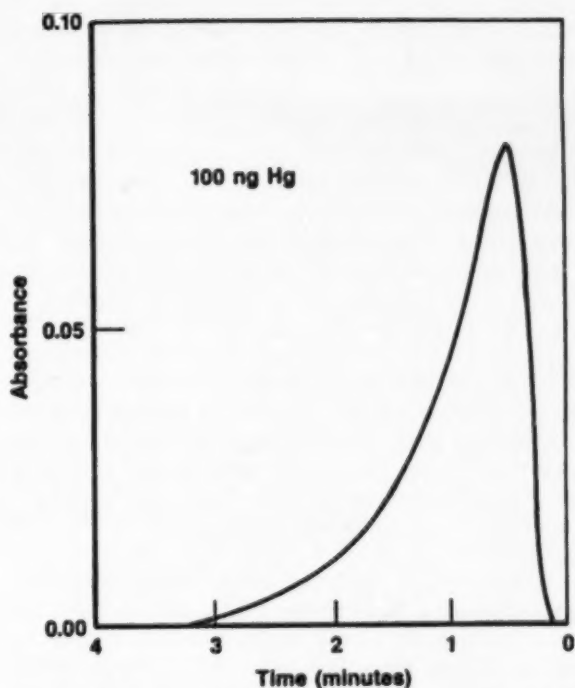


Fig. 3. Strip-chart recording of the absorbance profile for 100 ng mercury released from a 125-mL gas sparging bottle during the reduction-aeration step.

tion process has a significant influence on the absorbance peak height and profile. To allow comparisons of the results of this amalgamation method to other CV-AAS systems with spectrophotometers not capable of peak area measurements, all optimization experiments were designed to maximize the absorbance peak height.

As an initial point of reference, the nitrogen purge flow rate was adjusted to 540 mL/min, and the rate of mercury aeration from solution in the sparging bottle was determined. The experiment was conducted by removing the silver-wool plug from the silver-wool collection tube so that the mercury vapor aerated from solution was sent directly to a heated absorption cell. The absorption cell was heated by a portable incandescent lamp to prevent condensation of water vapor on the end-windows so as to provide an absorbance profile due only to mercury. The rate of mercury aeration from solution was determined as a function of continuous mercury absorption over the specified purge time. As illustrated in Fig. 3, the mercury vapor from a 100-ng mercury standard was quantitatively aerated from solution after purging of the 125-mL sparging bottle for three minutes. More than 90 percent of the mercury vapor was released after two minutes. A 2-minute reduction-aeration period represented a suitable compromise for maximizing the amount of elemental mercury for amalgamation within the shortest reduction-aeration time.

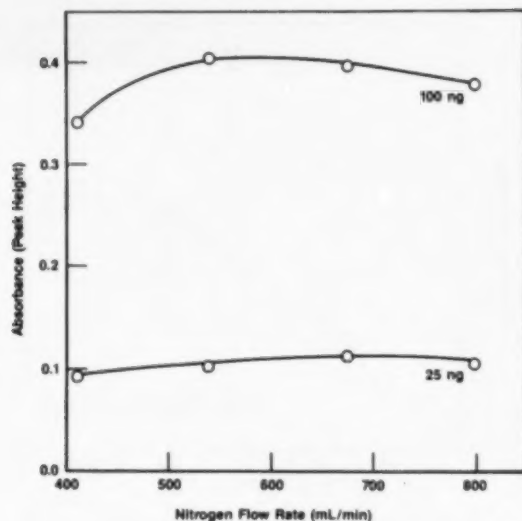


Fig. 4. Mercury absorbance as a function of nitrogen flow rate for the amalgamation CV-AAS method.

Based on the inherent assumption that at least 90 percent release of mercury from solution occurs at nitrogen flow rates greater than 540 mL/min, the nitrogen purge flow rate was optimized and tested for ruggedness with consideration only for the thermal desorption process. This experiment was conducted by using a 2-minute preconcentration time and with the Variac power supply set at 20 volts output; the nitrogen purge flow rate was varied from 410 mL/min to 800 mL/min. As illustrated in Fig. 4, comparable results were obtained for mercury standards of two different concentrations for flow rates between 540 mL/min and 800 mL/min; the nitrogen purge gas flow rate was considered rugged throughout this range. An operating flow rate of 540 mL/min was used for the subsequent experiments to test the ruggedness of the 2-minute preconcentration time and for optimization and ruggedness testing of the Variac power supply output.

Consistent with the goal to minimize analysis time, the ruggedness of a 2-minute preconcentration time was examined as a function of the variability of the observed mercury absorption measurement at different preconcentration times. A 0.7-g silver-wool plug was inserted in the collection tube, the Variac power supply was set at 20 volts output, and the nitrogen purge flow rate was maintained at 540 mL/min; the preconcentration time was then varied from 1 to 4 minutes. As illustrated in Fig. 5, a 2-minute preconcentration time was rugged at both high and low mercury concentrations for the mercury standards tested.

The Variac voltage output was briefly examined for optimization and ruggedness by maintaining the nitrogen purge gas flow rate at 540 mL/min and the preconcentration time at 2 minutes; the Variac voltage output

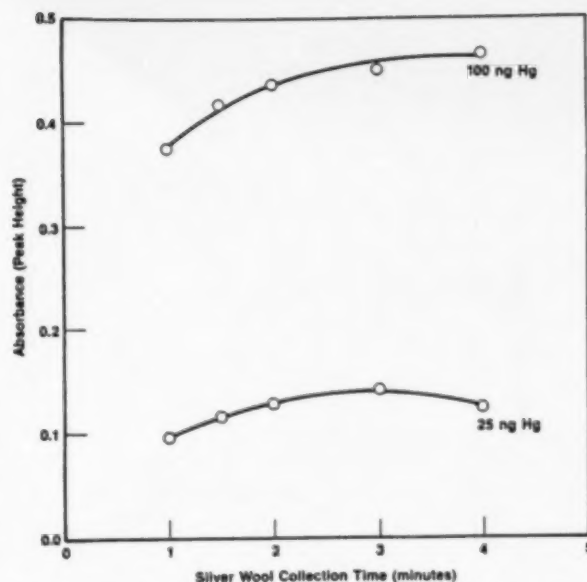


Fig. 5. Mercury absorbance as a function of preconcentration time for the amalgamation CV-AAS method.

was varied from 10 volts to 30 volts. The results of the analyses of two mercury standards as a function of the Variac voltage are illustrated in Fig. 6. At the 10 volt output setting, extensive broadening of the absorbance profile was observed; this broadening resulted in an extremely suppressed absorbance peak maximum. At the 15 volt output setting, absorbance peak broadening was less pronounced, but suppression of the peak maximum was still observed. At the 30 volt output setting, the Chromel-A wire overheated, as indicated by an orange glow in the wire, before the atomic absorption measurement was completed. The Variac output voltage was rugged and operationally safe in the 20 volt to 25 volt output range; the 20 volt output setting was retained as the optimal operating setting.

The fourth operating parameter, the weight of the silver-wool plug employed for the preconcentration of mercury, has been investigated in a previous study (Long, 1973). The previous results indicated that a 0.5-g to 1.0-g portion of silver wool used for preconcentration, when heated to 800°C before initial use, has a maximum loading capacity of 3 to 4 µg of mercury. The linearity of the customized amalgamation CV-AAS system, as discussed below, extends upward to an absolute mercury concentration of approximately 0.1 µg. Mercury breakthrough of the silver wool is not anticipated for mercury concentrations within the linear dynamic range of the amalgamation CV-AAS system. For analyses, 0.7-g silver-wool plugs were employed for the amalgamation process.

Detection limits

The instrumental detection limit for the amalgamation CV-AAS system was estimated from the standard

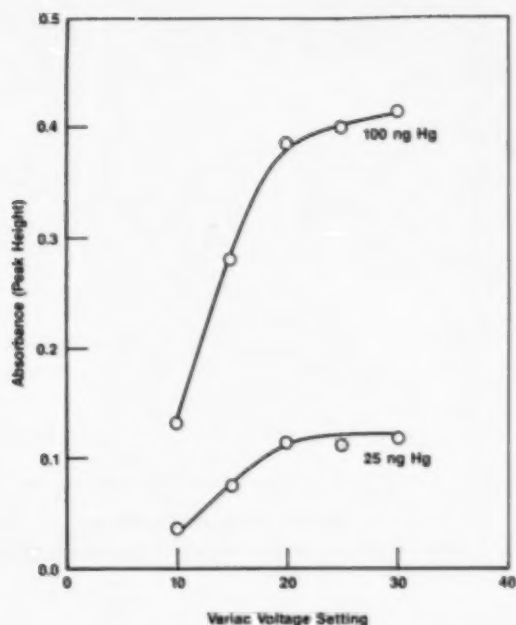


Fig. 6. Mercury absorbance as a function of Variac output voltage for the amalgamation CV-AAS method.

deviation of seven measurements of a $0.01\text{-}\mu\text{g}$ mercury standard diluted to 100 mL in the gas sparging bottle. By using the 3-sigma criterion, an absolute instrumental detection limit of approximately 1 ng (0.01 ng/mL for a 100-mL sample aliquot) was obtained. This represents approximately a 10-fold improvement in inherent detectability as compared to the recirculating CV-AAS system described in the current protocols of Methods 7470 and 7471. An instrumental detection limit of 10 ng (0.1 ng/mL for a 100-mL sample aliquot) was typically obtained with the recirculating CV-AAS system in this study.

Linear dynamic ranges

The linear dynamic range of the amalgamation CV-AAS system was determined by analyzing a series of mercury standard solutions ranging in concentration from 25 ng to 300 ng. The typical slope and linearity of the calibration curve for the amalgamation CV-AAS method is shown in Fig. 7. The linearity extends from the absolute instrumental detection limit of approximately 1 ng to 100 ng. This represents an intrinsic linear dynamic range of approximately 2 orders of magnitude of mercury concentration. The optimum concentration range for measurements using the amalgamation CV-AAS system was 10 ng to 100 ng. Although the linear dynamic range of the recirculating CV-AAS method also covered 2 orders of magnitude of mercury concentration, the linear region was shifted to higher mercury concentrations because of the lower sensitivity of the method. The recirculating CV-AAS

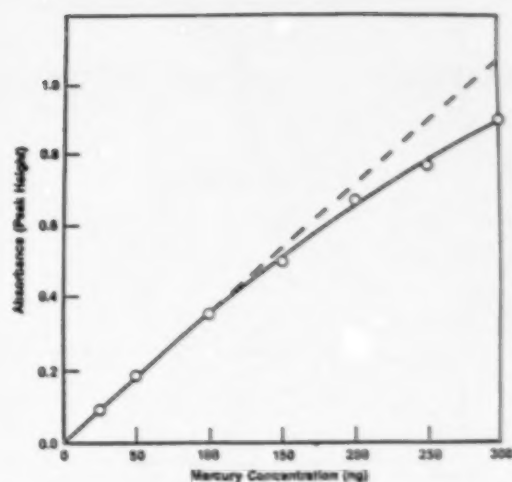


Fig. 7. Linear dynamic range for the amalgamation CV-AAS method.

system exhibited a linear response from the detection limit of 10 ng up to approximately $1\text{ }\mu\text{g}$. The optimum concentration range for measurements using the recirculating CV-AAS system was $0.1\text{ }\mu\text{g}$ to $1\text{ }\mu\text{g}$ of mercury.

Effects of dilutions

The higher intrinsic sensitivity of the amalgamation CV-AAS system requires dilutions of environmental samples containing relatively high mercury concentrations. Following the autoclave digestions of NBS-SRM 1645 (River Sediment) according to the procedure in Method 7471A, 5-fold and 10-fold dilutions of the sample digests were analyzed to verify that such dilutions would not have any adverse effects on the accuracy and precision of the measurements. An average mercury concentration of $1.21\text{ }\mu\text{g/g}$ with a relative precision of 4.6 percent was obtained for triplicate measurements of the 5-fold dilutions. An average mercury concentration of $1.16\text{ }\mu\text{g/g}$ with a relative precision of 4.7 percent was obtained for triplicate measurements of the 10-fold dilutions. The average mercury concentrations obtained for both dilution factors are in excellent agreement with the certified mercury concentration of $1.1\text{ }\mu\text{g/g}$ in NBS-SRM 1645. The precisions of triplicate measurements for both dilution factors are comparable, each being slightly less than 5 percent relative. These data indicate that dilutions of up to 10-fold have no adverse effects on the accuracy and precision of the amalgamation CV-AAS measurements.

Interferences

Correction for nonspecific background absorption. Water vapor and certain volatile organic species pro-

Table 3. Relative effects of volatile organic vapors on mercury measurements using recirculating CV-AAS and amalgamation CV-AAS.

Sample ^a	Recirculating CV-AAS Method		Amalgamation CV-AAS Method	
	Concentration Measured, $\mu\text{g/g}$	Percent Recovery ^b	Concentration Measured, $\mu\text{g/g}$	Percent Recovery ^b
NBS-SRM 1645	1.11 $\pm$ 0.068	101	1.19 $\pm$ 0.056 ^c	108
NBS-SRM 1645	2.41 $\pm$ 0.16	220	1.02 $\pm$ 0.049	93
+ 3- μL benzene				
NBS-SRM 1645	2.19 $\pm$ 0.064	200	0.91 $\pm$ 0.021	83
+ 1-mL MEK				

^a0.1-g test portions of NBS-SRM 1645; the certified concentration value for mercury is 1.1 $\pm$ 0.5 $\mu\text{g/g}$.

^bRelative to the average certified concentration value for mercury.

^cBased on six replicate measurements.

duce nonspecific absorption interferences which typically exhibit a continuum spectral distribution over the spectral bandpass; such spectral interferences can be conveniently compensated for automatically by using the deuterium arc lamp of the spectrophotometer. However, when use is made of the deuterium background corrector incorporated into most of the older commercial atomic absorption spectrophotometers including the Model 603 spectrophotometer used in the present study, the optical configuration is converted from a double-beam to a single-beam optical system. In single-beam operation, baseline shifts caused by long-term drifts in the mercury spectral lamp and deuterium arc lamp may occur. Detectability may be degraded by as much as 2-fold because of the low-frequency flicker noises from the mercury spectral lamp and the deuterium arc lamp (Zander, 1976). Moreover, the accuracy and precision of the background-corrected atomic absorption measurement with the deuterium arc lamp in most spectrophotometers degrade for nonspecific background absorption exceeding 0.5 absorbance unit (Sotera, 1982).

Volatile organics. Certain volatile organic compounds which remain in the sample digests following steam bath or autoclave digestions may absorb the primary mercury radiation at 253.7 nm during the atomic absorption measurement. Since nonspecific background absorption represents an additive interference, the method of multiple standard additions is not applicable. An additive interference must be eliminated prior to the atomic absorption measurement or it must be compensated for during the atomic absorption measurements by using an appropriate background correction scheme. However, Methods 7470 and 7471 for mercury do not specify the use of dynamic background correction techniques to compensate for nonspecific absorption interferences.

The on-line amalgamation/thermal desorption process eliminates nonspecific background absorption by

temporally separating the aerated mercury vapor from water and volatile organic vapors prior to the atomic absorption measurement. To demonstrate the advantage of the on-line amalgamation/thermal desorption process relative to the recirculating CV-AAS system without background correction, sample digests of NBS-SRM 1645 (River Sediment) spiked with volatile organic compounds were analyzed. Benzene and methyl ethyl ketone (MEK), which absorb mercury radiation at 253.7 nm, were selected as representative volatile organic compounds which may be present in environmental waste materials.

Test portions of NBS-SRM 1645 (River Sediment) were digested according to the autoclave procedure described in Method 7471A; aliquots of the sample digests were analyzed in triplicate by using both the recirculating and the amalgamation CV-AAS systems. Benzene and MEK spikes were added directly to the sample digests in the reduction-aeration vessel immediately prior to analysis. As indicated in Table 3, satisfactory mercury recoveries from the sample digests in the absence of benzene and MEK spikes were obtained by using both CV-AAS methods. However, in the presence of 3- μL additions of benzene, a 220-percent recovery was obtained with the recirculating CV-AAS system. A 200-percent recovery was obtained for mercury in the presence of 1-mL additions of MEK with the recirculating CV-AAS system. Mercury recoveries of 93 percent and 83 percent were obtained in the presence of benzene and MEK, respectively, when the amalgamation CV-AAS system was used. The average mercury concentrations measured in the sample digests of NBS-SRM 1645 containing benzene and MEK by amalgamation CV-AAS agreed, within the uncertainty limits, with the mercury concentrations measured for the sample digests in the absence of these volatile organic compounds.

The data in Table 3 indicate that certain volatile organic compounds in environmental sample digests

Table 4. Mercury spike recoveries by amalgamation CV-AAS using digestion procedures from U.S. EPA Methods 7470, 7471, and 7471A.

Sample (Digestion Procedure)	Average Percent Recovery of Hg Spike		
	Mercuric Chloride	Diphenyl Mercury	Methyl Mercuric Chloride
Simulated Aqueous Waste ^a (Method 7470)	—	125	113
Natural River Water ^b (Method 7470)	107	—	—
NBS-SRM 1646 ^c (Method 7471 Steam Bath)	86	100	93
NBS-SRM 1646 ^c (Method 7471A Autoclave)	96	107	97

^a50-mL samples spiked prior to digestion with 4.7 μg Hg as diphenyl mercury and 4.3 μg Hg as methyl mercuric chloride, respectively.

^b50-mL samples spiked prior to digestion with 0.02 μg Hg as mercuric chloride.

^c0.2-g samples spiked prior to digestion with 0.02 μg Hg as mercuric chloride, 0.95 μg Hg as diphenyl mercury, and 0.86 μg Hg as methyl mercuric chloride, respectively.

produce significant additive interferences in the recirculating CV-AAS measurements that result in a positive bias for the measured mercury concentration. The magnitude of the positive bias will be a function of the number of different volatile organic compounds in the sample digest as well as of their relative concentrations and molar absorptivities. When extrapolating our results for the recirculating CV-AAS method to equal spike additions of the two volatile organic compounds, benzene produced a nonspecific absorbance approximately 300-fold greater than that of MEK. Other volatile aromatic and carbonyl compounds, as well as chlorinated hydrocarbons, are also expected to produce nonspecific absorption interferences when the recirculating CV-AAS method is used.

The nonspecific background absorption interference caused by such volatile organic compounds may be automatically compensated for by using the deuterium arc background corrector if the spectrophotometer is equipped with one; however, the improvement in accuracy may be achieved at the expense of a degraded signal-to-noise ratio and increased imprecision at low mercury concentrations as discussed above. Because background correction with the deuterium arc lamp is not required when the amalgamation CV-AAS system described in this study is used, the Model 603 spectrophotometer is operated in a double-beam optical configuration which minimizes source-related noise. Volatile organic compounds in the sample digests are eliminated from the system prior to the mercury measurement by the on-line amalgamation/thermal desorption process. Therefore, by using the amalgamation CV-AAS system in which a deuterium arc background corrector is not required, double-beam absorption measurements of trace mercury concentrations in the presence of such volatile organic compounds may be performed with greater precision relative to single-

beam measurements in which deuterium arc background correction is employed.

Organomercuric compounds. The sample digestion procedures described in Methods 7470 and 7471 were tested for the recovery of mercury from aqueous and solid environmental sample matrices which had been spiked with diphenyl mercury and methyl mercuric chloride. One set of 50-mL portions of the simulated aqueous waste sample was spiked in triplicate with 4.7 μg Hg as diphenyl mercury and a second set was spiked in triplicate with 4.3 μg Hg as methyl mercuric chloride; the aqueous waste samples were then digested by the procedure in Method 7470. For comparison, one set of 50-mL portions of filtered river water was spiked in triplicate with 0.02 μg Hg as mercuric chloride and was then digested according to Method 7470. Two sets of 0.2-g portions of NBS-SRM 1646 (Estuarine Sediment) were spiked in triplicate with 0.95 μg mercury as diphenyl mercury and an additional two sets were spiked in triplicate with 0.86 μg mercury as methyl mercuric chloride; the solid samples were then digested by the steam bath and autoclave procedures described in Methods 7471 and 7471A, respectively. For comparison, two sets of NBS-SRM 1646 were spiked in triplicate with 0.02 μg Hg as mercuric chloride and were then digested according to Methods 7471 and 7471A. The sample digests were diluted appropriately and were analyzed by using the amalgamation CV-AAS system.

The results of the mercury recoveries from the inorganic and organic mercury spikes are presented in Table 4. By using the digestion procedure from Method 7470, the average mercury recoveries from diphenyl mercury and methyl mercuric chloride spiked in the simulated aqueous waste sample were 125 percent and 113 percent, respectively; the average mercury recovery from mercuric chloride spiked in the

river water sample was 107 percent. By using the steam bath and autoclave digestion procedures from Methods 7471 and 7471A, the average mercury recovery from the mercury compounds spiked in the reference sediment material ranged from 86 percent to 107 percent; no significant difference between the total mercury recovery from the inorganic and organic mercury compounds for the two digestion procedures was observed. The data in Table 4 indicate that mercury was completely recovered from the inorganic and organic mercury compounds tested under the experimental conditions when the digestion procedures from Methods 7470, 7471, and 7471A were used. Total mercury was completely recovered from the organomercurial spikes in the estuarine sediment by using Methods 7471 and 7471A which do not specify the addition of persulfate.

Inorganic matrix ions. Sulfide, copper, and chloride ions in environmental samples have been reported to interfere with CV-AAS measurements for mercury. The sample digestion procedure in Method 7470 and the amalgamation CV-AAS method were tested for potential interferences caused by these inorganic matrix ions. For the sulfide tests, triplicate 50-mL portions of the simulated aqueous waste sample were adjusted to pH 10 with sodium hydroxide before they were spiked with 2.0 mg sulfide from an aqueous solution of sodium sulfide. After the spiking, the samples were swirled and then were allowed to react for 15 minutes before proceeding with the sample digestion. The tests with copper(II) were conducted by spiking triplicate 50-mL portions of the simulated aqueous waste sample with 1.0 mg copper as aqueous copper nitrate. Triplicate 50-mL sample portions were also spiked with 3.4 g sodium chloride to test for a potential additive interference caused by the formation of chlorine gas during sample oxidation. Each sample aliquot, containing approximately 5.5 μg of endogenous mercury, was digested according to Method 7470; the sample digests were diluted 200-fold and then were analyzed with the amalgamation CV-AAS system.

The results of the tests for potentially interfering inorganic matrix ions are presented in Table 5. The results of the analyses for mercury in the presence of sulfide, copper, and chloride ions are in excellent agreement with the results of the analyses of the simulated aqueous waste sample with no inorganic matrix ion additions. The data indicate that no significant interference was observed for the simulated aqueous waste sample containing 40 mg/L sulfide, 20 mg/L copper(II), or 68 g/L sodium chloride.

The steam bath and autoclave digestion procedures in Methods 7471 and 7471A, respectively, were similarly evaluated for the recovery of mercury from NBS-SRM 1646 (Estuarine Sediment) in the presence of sulfide, cupric, and chloride matrix ions. However, based on the small number of replicates in each data

Table 5. Effects of selected inorganic matrix ions on mercury determinations in simulated aqueous waste digested by Method 7470 and analyzed by amalgamation CV-AAS.

Sample ^a	Concentration Measured, $\mu\text{g/L}$
Simulated Aqueous Waste	111 $\pm$ 3.0
Simulated Aqueous Waste + Sulfide (40 mg/L)	108 $\pm$ 1.5
Simulated Aqueous Waste + Copper (20 mg/L)	101 $\pm$ 0.6
Simulated Aqueous Waste + Chloride (68 g/L NaCl)	108 $\pm$ 2.5

^aThe endogenous Hg concentration in the simulated aqueous waste sample is approximately 110 $\mu\text{g/L}$.

set so that potential outlier data points could not be statistically treated, the limited data obtained by using Methods 7471 and 7471A could not be conclusively interpreted in regard to the extent of possible interferences from these inorganic matrix ions.

Analyses of solid environmental reference materials

The four reference sediment materials used in this study, which cover a 20-fold range of mercury concentrations, were digested by using the steam bath procedure from Method 7471 and were analyzed for mercury by using the amalgamation CV-AAS system. Concentration measurements with aqueous calibration standards were performed on the sample digests containing absolute mercury concentrations ranging from approximately 15 ng to 40 ng mercury; these absolute concentrations corresponded to three to eight times the reagent blank contamination level of approximately 5 ng mercury. The four reference sediment materials were also analyzed by the method of multiple standard additions (MSA); the sample digests were spiked with mercury as mercuric chloride at approximately 1X, 2X, and 4X (or 5X) the endogenous mercury concentrations in the respective sediment digests.

The results of triplicate analyses of the four reference sediment materials are presented in Table 6. The mercury recoveries based on the use of aqueous calibration standards ranged from 91 percent to 119 percent for three of the reference sediment materials; a marginally high recovery of 125 percent was obtained for the reference mercury concentration in NRCC BCSS-1. The determined mercury concentrations were within the certified or reference concentration range for each reference material except NRCC BCSS-1; a small positive bias of unidentified origin was obtained for mercury in this marine sediment reference material by using both calibration standards and the MSA method. The relative precision of the analyses ranged from approximately 1 percent to 7 percent.

Table 6. Mercury recoveries from reference sediment materials using Method 7471 steam bath digestions and amalgamation CV-AAS.

Sample	Concentration ($\mu\text{g/g}$)		
	Certified or Reference Value	Standard Calibration	Method of Multiple Standard Additions
NBS-SRM 1645	1.1 $\pm$ 0.5	1.19 $\pm$ 0.056	1.07 $\pm$ 0.15
NBS-SRM 1646	0.063 $\pm$ 0.012	0.075 $\pm$ 0.0053	0.063 $\pm$ 0.0069
NRCC MESS-1	0.171 $\pm$ 0.014	0.185 $\pm$ 0.0035	0.193 $\pm$ 0.0080
NRCC BCSS-1	0.129 $\pm$ 0.012	0.161 $\pm$ 0.0020	0.165 $\pm$ 0.0089

The results of the analyses using the method of multiple standard additions are also presented in Table 6. The comparable data obtained by analyses with aqueous calibration standards and by the method of MSA revealed that multiplicative interferences were not present in the CV-AAS measurement step for the determination of mercury in the reference sediment materials. The relative precisions of the analyses by the method of MSA ranged from 4 percent to 14 percent.

The four reference sediment materials were spiked in triplicate with mercury as mercuric chloride at concentration levels approximately equivalent to the respective certified or reference mercury concentrations. Following the digestions of the overspiked samples according to the steam bath procedure in Method 7471, the sample digests were analyzed by amalgamation CV-AAS. The average inorganic mercury spike recoveries for the four reference sediment samples ranged from 84 percent to 118 percent, and the relative precisions ranged from 7 percent to 15 percent. These data indicate that the steam bath digestion procedure in Method 7471 was satisfactory in recovering inorganic mercury from the four reference sediment materials.

Conclusions

The digestion procedures in Methods 7470 and 7471 were generally satisfactory for the complete recovery of endogenous mercury from the aqueous samples and the reference sediments tested, and for the recovery of total mercury from organomercurial spikes. Methods 7471 and 7471A generally provided comparable results for the digestions of reference sediment materials. However, the copious quantities of acids and reagents specified in the current digestion procedures contributed a reproducible reagent blank concentration of approximately 5 ng mercury as determined throughout this study by using the amalgamation CV-AAS system. Although 2-fold lower than the instrumental detection limit for the current U.S. EPA recirculating CV-AAS method, the 5 ng reagent blank level needs to be significantly reduced in order to fully realize the benefit from a CV-AAS method of higher intrinsic sensitivity when the present digestion procedures in Methods 7470 and 7471 are employed.

The greater inherent sensitivity of the amalgamation CV-AAS system over the recirculating CV-AAS system will extend the present testing capability to trace analyses of environmental hazardous waste digests containing absolute mercury concentrations as low as 1 ng when the reagent blank level is appropriately reduced. The amalgamation CV-AAS system has been successfully used for the accurate and precise analyses of environmental reference sediment digests containing trace mercury concentrations; absolute mercury concentrations that are only 1- to 4-times above the instrumental detection limit of the present EPA recirculating CV-AAS method have been measured. Furthermore, volatile organic species that are present in the sample digests and that produce nonspecific background absorption interferences with the recirculating CV-AAS system do not interfere with the mercury determinations conducted by using the amalgamation CV-AAS system. Water vapor and volatile organic species in the sample digests are eliminated prior to the mercury absorption measurement by the on-line amalgamation/thermal desorption process so that a deuterium arc background corrector is not required.

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